# Surface-modification enhanced semiconductor-insulator heteroepitaxy

B. R. Schroeder[1], Shuang Meng[1], A. Bostwick[1], E. Rotenberg[2] and M. A. Olmstead[1]

[1]Department of Physics, University of Washington, Seattle WA 98195, USA
[2]Advanced Light Source, Ernest Orlando Lawrence Berkeley National Laboratory,
University of California, Berkeley, California 94720, USA

## INTRODUCTION

To produce large band-offset (> 5 eV) quantum wells from Si and $CaF_2$ with atomically abrupt interfaces, it is necessary that the heteroepitaxy of $CaF_2$ on Si *and* that of Si on $CaF_2$ be well understood. Presently, only the growth of $CaF_2$ on Si(111) can be well controlled [1]. The epitaxy of Si on $CaF_2$ is hindered by (i) a very large surface energy difference and (ii) a strong chemical reaction between Si adatoms and surface fluorine. These factors have precluded growth of laminar silicon on $CaF_2$ with an atomically abrupt interface. Rather, growth at elevated temperatures is islanded, with Ca surface-segregation, while growth at low enough temperatures to avoid islanding results in an amorphous film. We used a combination of electron irradiation and surfactant introduction to combat both factors and achieve growth of laminar, crystalline Si on $CaF_2$.

We first electron-irradiated $CaF_2$ to remove surface fluorine, creating a high surface energy, Ca-terminated surface. This defected surface is extremely reactive. The reaction with water vapor is very strong and after only 1 hour at $10^{-10}$ mbar, a full monolayer of oxygen is present. To stabilize the surface against unwanted reactions, and, primarily, to introduce a surfactant for subsequent Si growth, this surface was then terminated with arsenic. Deposition of Si on this As-terminated surface in the presence of some additional $As_4$ resulted in ultra-thin (5ML), laminar, crystalline Si on $CaF_2$(111). We find Si-Ca interface bonds and a type-B interface (Si is rotated 180° with respect to the $CaF_2$). Further, the As behaves in true surfactant fashion and produces the well known 1x1 surface termination.

## As INTERACTION WITH $CaF_2$

We investigated $As_4$ interactions with pristine and irradiated $CaF_2$ to understand arsenic's proposed role as a surfactant to promote laminar Si growth on $CaF_2$. We find no As sticks to pristine $CaF_2$, at or above room temperature: defects are required. After electron irradiation to remove 1 monolayer (ML) fluorine, less than 1 ML of As is adsorbed on the surface (compared to Si(111):As). This may mean (a) As cannot reach sub-surface F vacancies and/or (b) the replacement of F by As is not one-to-one. At higher temperatures, more As is incorporated, primarily below the surface. Arsenic 3d photoemission displays two components, neither of which lies in bulk fluorine sites (see Fig. 1). The high binding energy peak
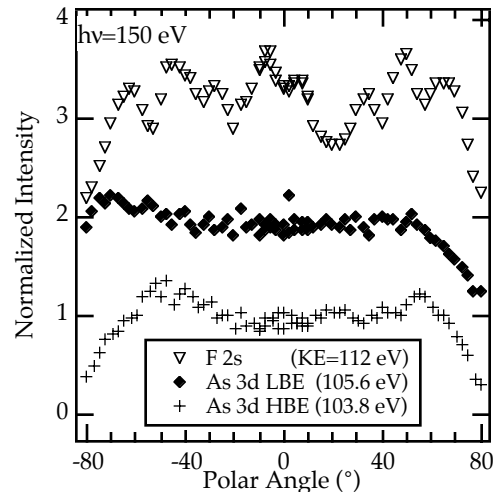


Figure 1: F and As Photoelectron diffraction from $CaF_2$ irradiated in the presence of $As_4$ at 370°C. Two distinct As components were observed. Neither lies in a buried F site.

shows weak XPD structure that is not modeled by sub-surface F sites, even after accounting for the different kinetic energies. The low binding energy peak is consistent with surface As, likely not in an ordered site. Our observation that the surface layer contains less than 1 ML As led us to grow Si on this surface in the presence of an $As_4$ flux.

## Si/CaF$_2$/Si INTERFACE AND OVERLAYER PROPERTIES

We deposited silicon on electron-irradiated and arsenic terminated $CaF_2$ in the presence of an arsenic flux at 500°C. The substrate was a thin (3.0 nm) layer of $CaF_2$ on a p-type Si(111) substrate to enable direct current heating and to reduce charging during photoemission. The arsenic-terminated silicon overlayer forms silicon-calcium interface bonds and completely wets the $CaF_2$. The deconvolved Si $2p_{3/2}$ spectrum at the left of Fig. 2 shows contributions due to the buried substrate (solid line) as well as the overlayer (dashed). Both contain an interface component shifted to lower binding energy, characteristic of Si-Ca bonding. The overlayer additionally shows Si-As bonding at the surface and some sub-surface As. The Fermi level at the top interface lies 0.3 eV closer to Si conduction band, perhaps reflecting the $n^+$ overlayer doping. XPD (Fig. 2, right) shows the local atomic structure is the same in the overlayer and substrate, as is the crystal orientation. The first $CaF_2$/Si interface is type-B, implying a similar 180° rotation at the upper interface. This is in contrast to the type-A orientation observed without surface modification. These results verify our predictions that this combination of electron irradiation and arsenic surfactant would lead to similar interface structure at the Si/CaF$_2$ and CaF$_2$/Si interfaces and promote laminar growth of Si nanostructures .
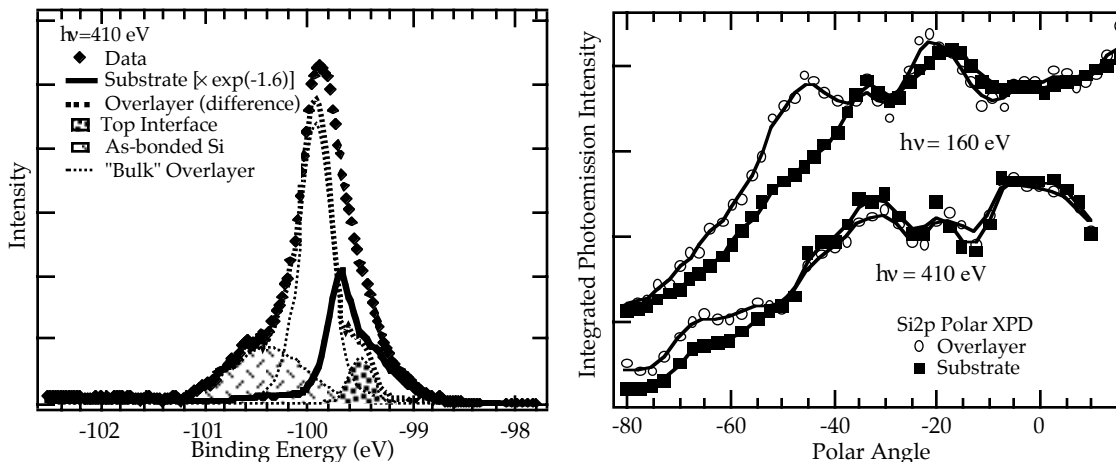


Figure 2. Si/CaF$_2$/Si(111) Film. Left: Deconvolved Si $2p_{3/2}$ spectrum. Substrate curve (solid) taken from CaF$_2$/Si(111) film. It was subtracted from the data to obtain Overlayer curve (dashed). Right: Photoelectron diffraction at surface (160 eV) and bulk (410 eV) sensitive photon energies for overlayer and substrate contribution ("substrate" also contains some overlayer contribution).

## PHOTON DAMAGE

Both electron and photon irradiation of $CaF_2$ have long been known to remove fluorine, and electron and photon irradiation cause similar effects on photoemission spectra. We used the high brightness and signal to noise ratio of the ALS to acquire spectra before oxidation changed the film, and also to monitor photon-induced changes in the film. We compared rates of photon-

stimulated fluorine desorption, and find electron-irradiated $CaF_2$ damages faster than pristine $CaF_2$ under similar conditions: initial defects promote further film erosion. Fortunately, we find Si- and As- covered $CaF_2$ are much more stable. A typical time variation of Ca 3p and F 2s emission from a pristine 1.0 nm thick $CaF_2$ film is shown in Fig. 3. As the fluorine is removed, Ca is converted from bulk $CaF_2$ to metallic Ca; interface Ca is not affected. The Ca and F photoemission intensity is reduced primarily in the "surface" peak (known to be on the high binding energy side of the bulk [1]).

We were able to obtain synchrotron-based XPD from $CaF_2$ films relatively unaffected by PSD by combining unidirectional defocusing of the beam and lateral movement of the sample in the narrow direction after each spectrum. All data shown above were obtained in that manner.

Figure 3: Photon-induced damage of $CaF_2$/Si(111). Top: Successive shallow core level spectra (~ 120 s/spectrum). Bottom: Time dependence at marked energies in top panel.

## ACKNOWLEDGEMENTS

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Principal investigator: Marjorie Olmstead, Department of Physics, University of Washington.
Email: olmstead@phys.washington.edu. Telephone: 206 543 7351.
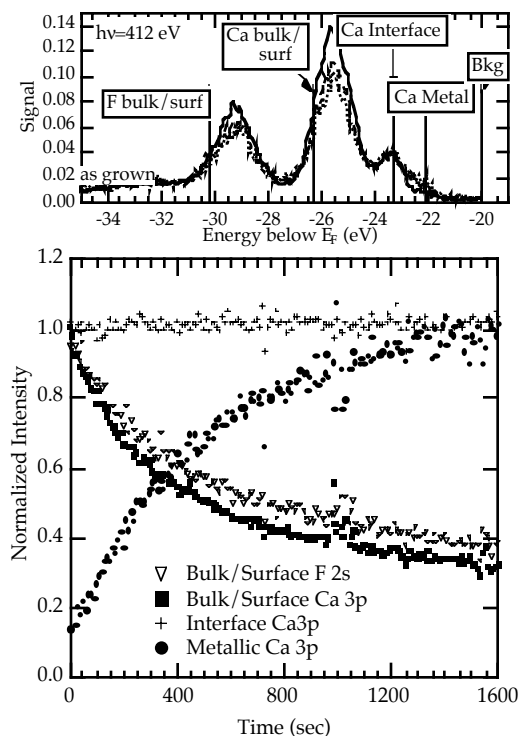Web Page: http://faculty.washington.edu/olmstd